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(54) PHOTOGRAPHIC LIGHT-SENSITIVE MATERIALS

(71) We, FUJI PHOTO FILM CO., LTD., a Japanese Company, of No. 210, Nakanuma, Minami Ashigara-Machi, Ashigara-Kamigun, Kanagawa, Japan, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to photographic light-sensitive materials, especially films, and coating compositions for their manufacture.

Photographic light-sensitive film is usually produced by coating a light-sensitive emulsion on a film base made of a material such as triacetyl cellulose or a polyester such as polyethylene terephthalate, which is electrically insulating, and hence the surface of the photographic film is substantially electrically insulating. It is, therefore, possible for static electric charge to accumulate on the film surface. Such charge may be formed in various ways, due to friction of the film surface with another portion of the film or with another material; such friction can occur by the loosening or tightening of the photographic film of a roll or its unrolling or rolling up, both during manufacture of the film or while it is in the camera, by friction of a sheet of X-ray film with the metal structure of an automatic camera, by movement of parts of a camera as in a cine camera, or by separation of the materials from contact with each other, such as a film and a sheet of fluorescent sensitizing paper in an automatic camera.

However it is caused, the resultant static charge is undesirable for the following reasons. When the charge has built up to a certain level, it can spontaneously discharge and thus has the effect of a localised exposure of the film; after development the discharges are visible as spotted branched or feather-like stains (known as "static marks"). These stains can greatly impair the photograph produced. Moreover, dust is attracted by the static charge and becomes attached to the film surface; this can directly impair the quality of the photograph and can also cause other difficulties such as unevenness of coating during manufacture.

The formation of the static charge is believed to be due to the ionic properties of the molecules of the contacting materials, but it has not at present been possible to forecast, from a knowledge of the chemical nature of these materials, whether a positive or negative charge will be formed.

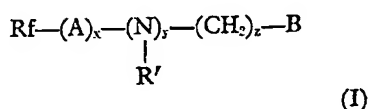
However, for preventing the accumulation of static charge, various proposals have been made for increasing the electrical conductivity of the surface of the photographic material so that the charge will leak away rapidly and not build up. For this purpose it has been proposed to increase the electrical conductivity of the support or of the surface of various of the coatings thereon, such as by incorporating various hygroscopic materials or water-soluble inorganic salts. However, these additives have insufficient antistatic effect and also have undesirable side effects. Synthetic surface active agents are known to be added to photographic coating compositions as wetting agents. British Patent Specification No. 1,259,398 describes and claims the use of certain perfluorocarbons as wetting agents. Some wetting agents have recently been tried as antistatic agents; they have been found effective for this purpose but are restricted in their action to particular types of coating compositions and ranges of concentration, and may be useless both as antistatic agents and as wetting agents in other compositions. It has, therefore, been necessary to use a variety of these surface active agents, according to the nature of the coating composition. These known surface active agents cause the surface of the material to acquire, upon friction, a positive static charge.

We have now found a class of surface active agents which have excellent antistatic action in various coating compositions. These agents have a fluorocarbon group as a hydro-

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phobic group in the molecule, and surfaces containing these agents acquire a negative static charge upon friction in the manner described above; and these agents have an excellent antistatic effect, even though the mechanism involved therein and the reason for the negative charge formation are not known

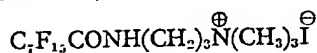
According to the present invention, a photographic material comprises a support, such as a film of synthetic plastics material, especially polyethylene terephthalate or triacetyl cellulose, having coated thereon at least one light-sensitive silver halide emulsion layer, and in a gelatino layer, especially a light-sensitive layer or a protective surface layer, there is incorporated a fluorocarbon compound of the following general formula:



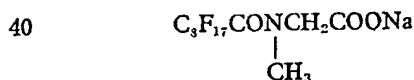
wherein Rf represents a perfluoroalkyl group having 4 to 12, preferably 6 to 8 carbon atoms; A represents the group $-\text{CO}-$ or $-\text{SO}_2-$ and x represents 0 or 1 when the fluorocarbon is cationic or A represents the group $-\text{CO}-$ and x represents 1 when the fluorocarbon is non-ionic or anionic; R' represents H or an alkyl group having 1 to 4 carbon atoms, y represents 0 or 1; z represents 0 or a positive integer less than 10; and B represents a water-solubilizing group such as a carboxylic acid group, a salt thereof, a sulphonic acid group, a salt thereof, or a quaternary ammonium group.

Typical examples of the fluorocarbon type surface active agents of this invention are shown below;

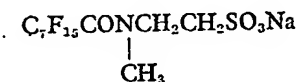
Compound I



Compound II



Compound III



The fluorocarbon type surface active agents to be used in this invention may be prepared using perfluoro-aliphatic carboxylic acid derivatives or perfluoro-aliphatic sulphonic acid derivatives as raw materials

according to general processes for producing surface active agents or the processes described in the specifications of U.S. Patents Nos. 2,809,990, 2,764,602, 2,593,737 and 2,567,011 and also in the Journal of the Chemical Society, 2574, 2640 (1957) and 2789 (1950), Journal of the American Chemical Society, 79, 2549 (1957) and "Industrial and Engineering Chemistry", 43, 2332 (1951)

The perfluoro-aliphatic carboxylic acid derivatives or perfluoro-aliphatic sulphonic acid derivatives used as the raw materials may be produced by the process described in the Journal of the American Chemical Society, 79, 2549 (1957), and the Journal of the Chemical Society, 2789 (1950), and 2574 and 2640 (1957).

An Example of the synthesis of the surface active agents used in this invention is given below.

Synthesis of Compound I

213 g. of (perfluoroheptane) carboxylic acid ethyl ester were dissolved in 100 ml. of ether and then 49.1 g. of N,N - dimethyl - trimethylene diamine were slowly added dropwise to the solution while maintaining the system at temperatures lower than 35°C. By distilling the reaction product mixture, N - (perfluoroheptanoyl) - N',N' - dimethyl - trimethylene diamine having a boiling point of 154-158°C was obtained. When the product was reacted with methyl iodide, compound I was obtained.

The same compound could be obtained similarly by using perfluoroheptane carbonyl-fluoride instead of (perfluoroheptane) carboxylic acid ethyl ester

The fluorocarbon surface active agent to be used in this invention may be added to any photographic gelatin layer of a photographic light-sensitive film, but particularly excellent results are obtained when the surface active agent is added to a surface gelatin layer.

The surface active agent of this invention may be used alone or together with saponin or another synthetic surface active agents known to be used as wetting agents in photographic coating compositions such as a sodium alkylbenzene sulphonate, a condensation product of naphthalene sulphonic acid and formalin, a sodium salt of an N - alkyltaurine or a sulphosuccinic acid ester.

Furthermore, it has been found that the fluorocarbon compounds are excellent not only as antistatic agents, but also as wetting agents in the coating of photographic layers on a support such as a film or a paper; that is to say, by adding the compound to a photographic emulsion layer or a gelatin layer, the wetting property of the coating composition is improved and the composition

can be coated uniformly on the support. The use of the fluorocarbon compound is particularly effective when photographic light-sensitive emulsion layers are applied in multiple layers, such as in the case of producing colour photographic films. If, in such case, the compound of this invention is added to the coating liquid for a surface protective layer, the coating liquid can be uniformly applied to a photographic emulsion layer that has been set by cooling but is still in the undried state.

The fluorocarbon surface active agent used in this invention may be added to a photographic emulsion or a gelatin-containing coating composition in an amount of 0.05—100 g. preferably 0.1—0.5 g. per kilogram of the emulsion or coating composition. This amount is considerably less than the amount needed of a surface active agent known in the art as a coating aid.

The behaviour and the mechanism of the surface active agent of this invention have not yet been clarified but it is believed that the antistatic property of the photographic film is increased by the improvements in conductivity, slidability of the surface film, and dielectric constant thereof.

The advantages obtained by the use of the fluorocarbon compound according to this invention are summarised below.

1) When a photographic material according to this invention is subjected to friction with another material in any of the ways described above, its surface becomes charged negatively, and very little, if any, static charge accumulates.

Moreover, when the fluorocarbon compound is used together with another surface active agent which also has an antistatic effect, a multiplied effect is obtained; when the fluorocarbon compound is used together with another surface active agent having no antistatic effect, the antistatic effect of the fluorocarbon compound is not reduced. By contrast, if a conventional surface active agent having some antistatic effect is used together with another (non-antistatic) surface active agent, the antistatic effect is reduced or eliminated in most cases.

2) A surface layer containing the fluorocarbon compound has reduced hygroscopicity, improved surface, smoothness and slidability and increased stability of the electrical resistance of the surface.

3) The surface tension of a coating composition containing the compound of this invention is greatly reduced, and thereby very uniform coating is obtainable even at high coating speeds. In general, it is necessary in the case of multiple layer coating that the surface tension of a coating composition for a photographic layer be lower than that of a coating composition for a photographic layer positioned below the first-mentioned

photographic layer. In particular, since a colour photographic emulsion customarily contains as an emulsifying agent for a coupler a surface active agent which greatly reduces the surface tension of the emulsion, the surface tension of a coating composition for the surface layer must be lower than that of the colour photographic emulsion, which renders difficult the selection of a surface active agent for the surface coating composition. The addition of a small amount of the fluorocarbon surface active agent can reduce the surface tension of a coating composition to about 23 dynes/cm.

4) When a photographic light-sensitive material of this invention is developed, especially by an automatic process, practically no scum or foam is formed.

When saponin or a conventional surface active agent is used as wetting agent in the material, foam or scum is frequently formed, whereby unevenness is formed on the finished image, which is an especially serious problem when it occurs in medical or industrial X-ray films.

5) The fluorocarbon compound does not impair the photographic properties of the material, such as sensitivity, fog or contrast.

The invention will be further illustrated by the following examples, wherein percentages are by weight, and which relate to black-and-white negative film, including X-ray film.

EXAMPLE 1

A silver chlorobromide photographic emulsion containing 7% gelatin and 5% silver halide was prepared. To this emulsion was added a 10% aqueous solution of saponin in an amount of 5 ml. per one kilogram of the photographic emulsion. The resultant photographic silver halide emulsion was applied to a subbed triacetyl cellulose film and after setting the emulsion layer thus formed by cooling, a gelatin solution containing 20 ml. of a 1% aqueous solution of the aforesaid Compound I and 40 ml. of a 10% aqueous solution of saponin in one kilogram of 2% aqueous gelatin solution was applied to the silver halide emulsion layer. The layer was set by cooling and then dried.

Uniform coating of the surface layer was obtained without the formation of strains or unevenness. The antistatic property of the film was tested as follows:

The film was placed on a fluorescent sensitizing paper and after rubbing the film or the paper with a roller under the conditions of 23°C and 50% RH to cause a prescribed amount of friction, the fluorescent sensitizing paper was separated from the film and then the X-ray film was developed for 4 minutes at 20°C using a developing liquid having the following composition:

	Warm water (50°C)	700 ml
	N - methyl - p - aminophenol sulphate	4 g.
	Anhydrous sodium sulphite	60 g.
5	Hydroquinone	10 g.
	Sodium carbonate monohydrate	53 g.
	Potassium Bromide	2.5 g.
	Water to make	1 litre

Almost no static marks were observed.

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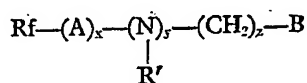
EXAMPLE 2

A highly sensitive X-ray photographic emulsion containing 9% gelatin and 9% silver iodobromide was prepared. To this emulsion were added 5 ml. of a 4% aqueous solution of saponin per one kilogram of the emulsion. The resultant photographic emulsion was applied to a subbed triacetyl cellulose film and then, without setting the emulsion layer by cooling, a gelatin solution containing 20 ml. of a 1% aqueous solution of Compound II and 30 ml. of a 5% aqueous solution of saccharose-dodecenyl succinic ester in one kilogram of 2% aqueous gelatin solution was applied to the photographic emulsion layer.

The gelatin solution could be coated without the formation of stains or unevenness. When antistatic property of the film was tested by the manner described in Example 1, almost no static marks were observed and also it was confirmed that the results were better than in the case of using saccharose - dodecenyl succinic ester alone. Also, when 5 ml. of 5% aqueous solution of a sodium salt of N - oleoyl - N - methyltaurine was added instead of the solution of Compound II, more static marks were formed than in the case of using saccharose - dodecenyl succinic ester alone.

WHAT WE CLAIM IS:—

1. A photographic material comprising a support having thereon at least one light-sensitive silver halide emulsion layer, said material having incorporated in a layer containing gelatin a fluorocarbon compound represented by the following general formula:



(I)

wherein Rf represents a perfluoroalkyl group having 4 to 12 carbon atoms, A represents the group —CO— or —SO₂— and x represents 0 or 1 when the fluorocarbon is cationic or A represents the group —CO— and x represents 1 when the fluorocarbon is non-ionic or anionic, R' represents H or an alkyl group having 1 to 4 carbon atoms, y represents 0 or 1, z represents 0 or an integer less than 10, and B represents a water-solubilizing group.

2. A photographic material as claimed in Claim 1, wherein B represents a carboxylic acid group or a salt thereof, a sulphonic acid group or a salt thereof, or a quaternary ammonium group.

3. A photographic material as claimed in Claim 1 or 2, wherein the fluorocarbon compound is contained in a light-sensitive silver halide gelatino layer.

4. A photographic material as claimed in Claim 1 or 2, wherein the fluorocarbon compound is contained in a protective surface layer.

5. A photographic material as claimed in any preceding claim, wherein the fluorocarbon compound is present in the layer in an amount of 0.05 to 100 grams per kilogram of the emulsion or coating composition used to make the layer.

6. A photographic material as claimed in Claim 5, wherein the fluorocarbon compound is present in an amount of 0.1 to 0.5 grams per kilogram.

7. A photographic material as claimed in any preceding claim, wherein another surface active agent is present in the layer containing the fluorocarbon compound.

8. A photographic material as claimed in Claim 7, wherein said other surface active agent is a sodium alkylbenzene sulphonate, a condensation product of naphthalene sulphonic acid and formalin, a sodium salt of an N - alkyl - taurine or a sulphosuccinic acid ester.

9. A photographic material as claimed in any preceding claim, wherein the fluorocarbon compound is any of the Compounds I to III hereinbefore set forth.

10. A photographic material as claimed in any preceding claim, wherein the support is a film made of triacetyl cellulose or a polyester.

11. A photographic material as claimed in Claim 1, substantially as hereinbefore described in any of the foregoing Examples.

12. A coating composition for use in pre-

paring a photographic material as claimed
in any preceding claim, which comprises an
aqueous gelatin solution containing a fluoro-
carbon compound as defined in Claim 1, 2
5 or 9.

13. A composition as claimed in Claim
12, wherein the solution is a silver halide
gelatino emulsion.

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